Project # FC-041: Novel Approach to Advanced Direct Methanol Fuel Cell Anode Catalysts

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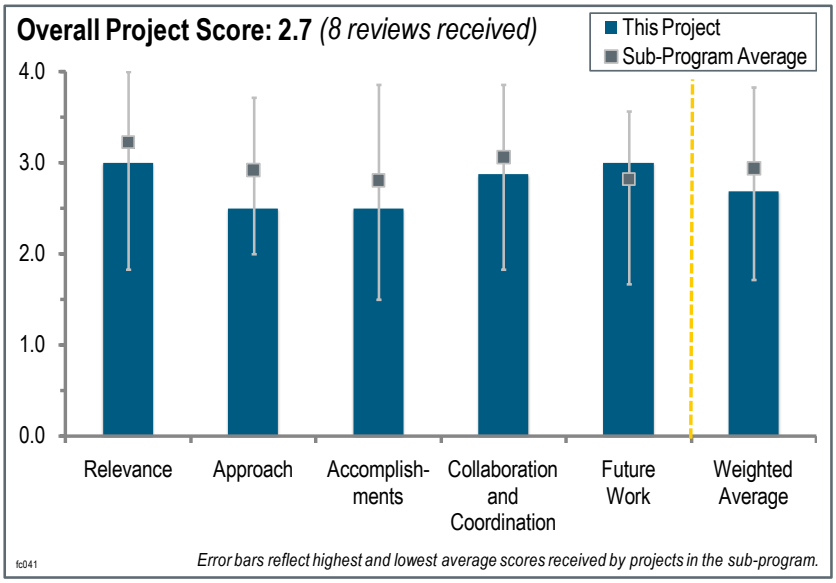
Brief Summary of Project:

The overall objective of this project is to develop and demonstrate direct methanol fuel cell (DMFC) anode catalyst systems that meet or exceed the U.S. Department of Energy's (DOE) 2010 targets for consumer electronics applications. The specific goal is to improve the catalytic activity and durability of the platinum-ruthenium (PtRu) for the methanol oxidation reaction via optimized catalyst support interactions. A similar approach for oxygen reduction reaction (ORR) catalysis is advantageous for both DMFC and hydrogen fuel cells.



Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.0** for its relevance to DOE objectives.

- The proposed effort is targeted at DMFC anode performance and durability, which should help address the portable power lifetime goals. If the investigators can demonstrate improvements in performance for practical catalysts at a reasonable cost and production rate that can be implemented into a membrane electrode assembly (MEA), the work should address the cost targets.
- Improving the performance of the anode catalyst in DMFC systems is critical to achieving the DOE technical targets. With that said, it is not clear how this work will impact the effort to reach those goals. The investigators did not present any data on how this catalyst impacts the MEA performance (although MEA testing is planned for later this year).
- The objectives are consistent with required improvements in cost, performance, and durability.
- The project is directly relevant to DOE objectives, as it addresses three important limitations of state-of-the-art DMFCs: (1) the low catalytic activity of PtRu for the methanol oxidation reaction, (2) the low durability of the anodic PtRu catalyst, and (3) the high costs depending on the high loading of expensive Pt and PtRu-catalysts used.
- The project is relevant in that it focuses on an important aspect of DMFC technology (i.e., the anode catalyst). The DOE objectives are stated, but the milestones for the project are largely activities, rather than quantitative metrics that can be related to the DOE goals.
- DMFCs are part of DOE's strategy for the commercialization of fuel cells, but this project does not directly address the biggest problems with DMFCs—methanol crossover through the membrane and Ru dissolution from the anode, and the subsequent poisoning of the cathode by this Ru. Improving the evenness of the dispersion of alloy catalyst particles, which is the major advance promised by this project, is of more general potential in the DOE Hydrogen and Fuel Cells Program versus specifically in DMFC research and development. For ORR catalysts, it has proven more difficult to get even dispersion of Pt-alloy particles on corrosion resistant carbon (including Vulcan, which is more corrosion resistant than the Ketjen black or HSC [sic] on which alloys give highest activity) than it has been for pure Pt particles. Therefore, the methods of this project could be quite beneficial in combining high-activity Pt-alloy ORR catalysts with corrosion resistant carbon supports.
- Investigators did not conduct a cost analysis, which seems like a big omission. Surely a rough calculation would show whether this approach will meet the cost goals.

Question 2: Approach to performing the work

This project was rated **2.5** for its approach.

- The overall development approach seems to be quite sound. The work needs to continue toward measurements of catalyst performance and durability in a real MEA using a reasonable system with compatible operating conditions, including some tolerance for off specification operation such as low methanol concentration (partial fuel starvation) operation.
- The methods seem fine, but the logic behind them is problematic. If the PtRu is held on the carbon by the nitrogen groups on the surface, surely the nitrogen is protonated under normal operating conditions. This reviewer wants to know if the density functional theory (DFT) calculations address this issue, and if there is any basis in the literature.
- The authors followed a productive pathway to apply an advanced concept to practical carbon-black-supported catalysts. They first demonstrated their concept on highly-ordered pyrolytic graphite (HOPG), on which the ion implantation was easy, and then made the new equipment needed to do the ion implantation and sputtering coating on powders. This method is an ingenious and potentially productive approach to using line-of-site deposition techniques to coat all sides of powder particles. The use of DFT calculations to draw conclusions about the relative solubility of Pt and Ru from non-implanted versus implanted carbon supports is perhaps a bit questionable, as it appears to have been done by just calculating the energy to remove one atom (either Ru or Pt) from a particular four-atom Pt_2Ru_2 cluster. One would expect the dissolution energies to vary significantly with particle size, geometry, and composition.
- The approach to improve interactions with support has some merit, but it is unlikely to make significant gains due to the inherent instability of Ru in the DMFC conditions.
- It is not clear if a 20%–30% improvement in methanol oxidation reaction (MOR) half-cell activity will reduce the overall costs for a DMFC. A comparison of catalyst costs made by HOPG and sputtering methods for large quantities will be helpful.
- Doping of the carbon support with nitrogen appears to decrease the degradation of the electrocatalyst by nanoparticle migration and coalescence. However, one of the major mechanisms of loss of MOR activity is the leaching of Ru from PtRu alloy catalysts. The DFT calculations indicate that nitrogen doping will actually increase the tendency of Ru to leach from the alloy. The responses to reviewer comments are conflicting regarding the effect of nitrogen doping on Ru leaching.
- The main thrust of the project is the catalyst and support structure. A lot of experimental and theoretical effort has been spent on the HOPG system. This reviewer wants to know how relevant this material is to the types of carbon that are actually used as catalyst supports in the DMFC. The durability improvements realized for HOPG after ion implantation are not unexpected, given the nature of the material.
- This reviewer's chief complaint of the approach is that no MEA testing has occurred and the project is near completion. There is no time to learn from the MEA testing, which would have allowed critical information to be fed back into the development process.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.5** for its accomplishments and progress.

- The project has made good progress toward the catalyst goals, and continued testing in an MEA configuration is important. This testing will also help to understand the performance and durability performance benefits against the potential costs associated with the catalyst.
- The test data presented appeared to indicate improved catalyst activity. Again, the investigators did not present any data from MEA testing, so it is unknown how it will improve cell performance. Also, the investigators presented only minimal degradation information.
- The investigators have made good progress on understanding the process parameters to get either durability or performance improvements. The improvements are incremental, rather than significant, and may not justify the significant efforts on developing the processing parameter understanding. The balance appears to be off between optimizing processing parameters versus determining clear indications of potential improvements and the ability to meet targets. The stability of the Ru is a critical component, but the only stability test to date has

measured only the electrochemical surface area (ECSA) change. The investigators are already 80% into the project, and this is very late for not having this information.
- The researchers have made good progress in determining the effect of various deposition parameters on methanol oxidation activity in half-cell measurements. Though ECSA losses are lower for nitrogen-doped, carbon-supported materials versus undoped carbon support, the losses are still unacceptably high. The cell voltages are extremely low.
- The accomplishments of the project in terms of synthesis and physical characterization of the catalysts are good, but it is too late in the project for the electrochemical work to be in such an early state. Slide 13 claims a 20%–30% improvement in MOR activity for the implanted-support catalysts. Given the difficulties in measuring electrocatalytic activities, it is unclear whether such a gain is significant—one needs bigger effects to be sure. The conclusions from the DFT suggest that the net effect of the implantation may be negative for DMFCs, per the statement on slide 30 that "[Ruthenium] is more susceptible to preferential leaching from PtRu over the [nitrogen]-implanted carbon than over unmodified carbon"—a statement that appears consistent with the results for pyridinic nitrogen on slide nine. Slide 31 appears to give a contradictory statement—"[Ruthenium] is stabilized by the presence of [nitrogen]"—which probably refers only to the pyrollic nitrogen on slide nine. The investigators appear to recognize at least part of the potential importance of their work to ORR (though the presenter did not mention the greater problems with dispersion of the Pt alloy than with pure Pt particles). However, the only ORR data presented (slide 24) shows an anomalously low ECSA and mass activity for Pt on the nitrogen-implanted carbon. That slide claims enhanced activity for Pt on the nitrogen-doped carbon, but only the specific activity, not the more important mass activity, is enhanced. On the positive side, the researchers do appear to have demonstrated improved durability against potential cycling for their MOR catalysts.
- A large effort has been made with nitrogen-doped carbon-supported PtRu catalysts regarding durability. Normally, MEAs with high-loaded PtRu catalysts are used in commercial DMFCs. It would be better to also compare the in-house catalyst with HiSpec 12100 from Johnson-Matthey Fuel Cells Inc. (JMFC). There is no information on how the nitrogen-doped carbon support will decrease the corrosion of Ru or Ru oxide from the catalyst. This is only done for Pt.
- Durability and performance have improved, but it is unclear why. This seems a little too much like alchemy. Also, the project is really not improving on the generally low performance of the anode in DMFCs.
- The new materials being developed here seem to have a similar performance to JMFC's commercial JM5000 catalyst. There are no error bars associated with the numbers, and electrode preparation could introduce enough variability to make the differences small, if not insignificant. The micrograph on slide 14 shows only the catalyst after 5,000 cycles. It would be useful to compare these results with the original un-cycled sample, as well as the other catalysts studied.

Question 4: Collaboration and coordination with other institutions

This project was rated **2.9** for its collaboration and coordination.

- The project demonstrates good collaboration between the participants.
- The project features good collaborations, although Mechanical Technology, Inc. does not appear to be very involved.
- The institutions and each of their roles were given. It appears that the group is working well together.
- The collaboration between the parties appears to be good.
- The project has lots of collaboration, but it seems that the presenter does not know what the collaborators are all doing.
- Though many collaborators were listed, it is unclear what they have contributed to the project in the past year.
- There is no indication of collaboration with BASF (the state-of-the-art catalyst is from JMFC).

Question 5: Proposed future work

This project was rated **3.0** for its proposed future work.

- The continued testing of the MEA in a practical fuel cell configuration to measure the durability and performance benefits under real DMFC operating conditions is important. This testing should be evaluated against the potential additional costs associated with catalyst synthesis and production at a reasonable scale.
- The MEA testing will be beneficial.
- The plans for finishing off the project are fine, and in line with past activities. The beam time at the Stanford Linear Accelerator Center will add more data. It is unclear whether this information is useful.
- It is very important to better understand these catalyst systems under fuel cell conditions. The composition of the catalyst after operation and voltage cycling needs to be determined.
- The future work plan is reasonable. Understanding the amorphous components of these materials is important, and will be addressed. X-ray diffraction studies only provide some of the story. The investigators have planned more MEA and DMFC performance studies with the new catalysts, which will be useful in determining the value of this approach.
- Establishing the "catalyst degradation mechanisms, e.g., extent of Ru dissolution and catalyst coarsening" should be the highest priority of the project, and will help determine if the nitrogen doping is preventing degradation of the chemical composition of the MOR catalyst. Testing full cells should also be one of the highest priorities.
- The project is largely completed, so a major shift in plans—such as directing the work to the stabilization of Pt alloy particles on corrosion resistant carbon for ORR—would be unrealistic, though it would improve the contributions of the project to the overall Program. The remaining work should be directed toward a continued search for large activity gains (not 20%), experimental quantization of the effects of nitrogen doping on Ru dissolution from PtRu, and a bit more exploratory work on ORR catalysts to see if a mass activity gain from nitrogen implantation can be demonstrated (larger advantages would be expected from supports more highly graphitized than Vulcan).
- There are milestones missing.

Project strengths:

- This project features good catalyst development and characterization, in particular the ex-situ characterization.
- The project is well structured, and has clear plans. The approach showed good increases in catalyst support interactions, as well as some improvements in activity, but not in the same design. The project has moved from model systems to viable project supports.
- The project partners have great experience and expertise in their respective fields.
- The deposition method appears to result in highly-dispersed nanoparticles.
- This is a good team that has the resources to perform the proposed work.
- The project features a rational pathway to improve the evenness of dispersion of Pt and Pt alloy particles on corrosion resistant carbon supports. Another project strength is the nice implementation of line-of-sight implantation and coating of powder supports. The project team demonstrated improvements of particle stability against voltage cycling.

Project weaknesses:

- The project needs to include more testing in an MEA using a set of reasonable characteristics for the MEA. The project team should also perform more testing using system compatible conditions.
- One weakness is the limited opportunity to learn from MEA testing and feed the data back into the development process. Also, there is minimal time to evaluate any degradation issues.
- The project is really empirical, and uses facilities that are in place but without sound rationales as to why they would work.
- One area of weakness of this project is the lack of understanding of how a catalyst system behaves in the MEA and under relevant conditions.
- One major degradation mechanism is Ru leaching from the alloy. Therefore, the Ru leaching should be measured—for example, with methanol stripping for both catalysts (commercial and in-house made) after 5,000

cycles. Methanol stripping experiments for the cathode would also be helpful to indicate leached Ru that is permeated through the membrane.
- The lack of focus on Ru leaching degradation is an area of weakness.
- The project needs a better focus, which works backwards from the DOE goals. It may have been covered in a previous review, but the amount of effort spent on HOPG studies is questionable. The project involves interesting work, but it may not have much relevance to real-world support materials that are used in fuel cells. Error bars and better statistics are needed to establish what is significant and what is not.
- One area of weakness is the dubious improvements versus the main catalyst durability challenge of DMFCs. Another weakness is the Ru dissolution from the anode and deposition on the cathode. The DFT results would need at least a study of the sensitivity of the conclusions to PtRu cluster size and shape before one could place any credence in them. The project devotes insufficient attention to ORR, where the benefits of this approach would likely be the greatest, even for DMFCs.

Recommendations for additions/deletions to project scope:

- Investigators should conduct an objective assessment of possible gains with continued optimization of processing conditions to determine the value of continuing the activity.
- Researchers should compare the in-house catalyst in real MEAs with commercial MEAs—for example, from JMFC—with improved PtRu catalysts.
- The project team should consider dropping implantation of other materials in order to concentrate more on the nitrogen implantation work. The team should also check the sensitivity of DFT conclusions to PtRu cluster size and shape, and consider MOR steady-state activity measurements in addition to cyclic voltammograms. Additionally, the researchers should do a bit more work on ORR, preferably with more supports that are more highly graphitized than Vulcan. While doing these studies with Pt-alloy (e.g., Pt_3Co) particles is probably not realistic in this project, one could get relevant information by using pure Pt particles, but then annealing to an alloy-formation-like 900°C in 3% H_2/N_2 to presinter the particles before starting to study the resistance of the catalyst to voltage cycling.